A NEW APPROACH TOWARDS PROPERTY NANOMEASUREMENTS USING IN-SITU TEM

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ABSTRACT

Property characterization of nanomaterials is challenged by the small size of the structure because of the difficulties in manipulation. Here we demonstrate a novel approach that allows a direct measurement of the mechancial and electrical properties of individual nanotube-like structures by in-situ transmission electron microscopy (TEM). The technique is powerful in a way that it can directly correlate the atomic-scale microstructure of the carbon nanotube with its physical properties, providing an one-to-one correspondence in structure-property characterization. Applications of the technique will be demonstrated on mechanical properties, the electron field emission and the ballistic quantum conductance in individual nanotubes. A nanobalance technique is demonstrated that can be applied to measure the mass of a single tiny particle as light as 22 fg (1 f = 10^{-15}).

INTRODUCTION

Characterizing the properties of individual nanostructure is a challenge to many existing testing and measuring techniques because of the following constrains [1]. The size (diameter and length) is rather small, prohibiting the applications of the well-established testing techniques. The small size of the nanostructures makes their manipulation rather difficult, and specialized techniques are needed for picking up and installing individual nanostructure. Therefore, new methods and methodologies must be developed to quantify the properties of individual nanostructures. Among the various techniques, scanning probe microscopy (STM, AFM) has been a major tool in investigating the properties of individual nanostructures.

We have recently developed a novel approach which uses in-situ transmission electron microscopy (TEM) [2,3] as an effective tool for measuring the properties of individual carbon nanotubes. This is a new technique that not only can provide the properties of an individual nanotube but also can give the structure of the nanotube through electron imaging and diffraction, providing an ideal technique for understanding the property-structure relationship. The objective of this paper is to review our recent progress in applying in-situ TEM for characterizing the electrical, mechanical and field emission properties of carbon nanotubes, aiming at pointing out a new direction in nanomeasurements.

EXPERIMENTAL METHOD

TEM is a powerful tool for characterizing the atomic-scale structures of solid state materials. A powerful and unique approach could be developed if we could integrate the structural

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information of a nanostructure provided by TEM with the properties measured from the same nanostructure by in-situ TEM. Thus, an one-to-one correspondence can be achieved, providing a model system for comprehensively understanding nanomaterials. To carry out the property measurement of a nanotube, a specimen holder for an JEOL 100C TEM (100 kV) was built for applying a voltage across a nanotube and its counter electrode [4]. The nanotube to be used for property measurements is directly imaged under TEM (Figure 1), and electron diffraction patterns and images can be recorded from the nanotube. The information provided by TEM directly reveals both the surface and the intrinsic structure of the nanotube. This is a unique advantage over the SPM techniques. The static and dynamic properties of the nanotubes can be obtained by applying a controllable static and alternating electric field. The nanotubes were produced by an arc-discharge technique, and the as-prepared nanotubes were agglomerated into a fiber-like rod. The carbon nanotubes have diameters 5 - 50 nm and lengths of 1- 20 μm and most of them are nearly defect-free. The fiber was glued using silver past onto a gold wire, through which the electrical contact was made. The counter electrode can be a droplet of mercury or gallium for electric contact measurement or an Au/Pt ball for electron field emission characterization.

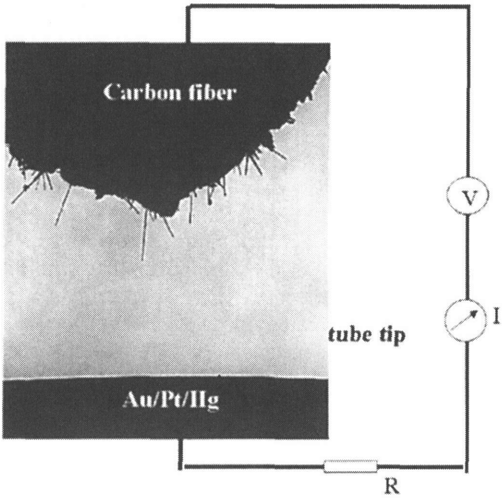


Fig. 1. TEM image showing carbon nanotubes at the end of the electrode and the other counter electrode. A constant or alternating voltage can be applied to the two electrodes to induce electrostatic deflection or mechanical resonance.

EXPERIEMENTAL RESULTS

Bending modulus of a carbon nanotube

To measure the bending modulus of a carbon nanotube, an oscillating voltage is applied on the nanotube with ability to tune the frequency of the applied voltage. Resonance can be induced in carbon nanotubes by tuning the frequency (Figure 2). Resonance is nanotube selective because the natural vibration frequency depends on the tube outer diameter (D), inner diameter (D_1), the length (L), the density (ρ), and the bending modulus (E_b) of the nanotube [5]:

$$\nu_i = \frac{\beta_i^2}{8\pi}\frac{1}{L^2}\sqrt{\frac{(D^2+D_1^2)E_\beta}{\rho}} \quad (1)$$

where β_1 = 1.875 and β_1 = 4.694 for the first and the second harmonics. After a systematic studies of the multi-walled carbon nanotubes, the bending modulus of nanotubes was measured as a function of their diameters [2]. For nanotubes produced by arc-discharge, which are believed

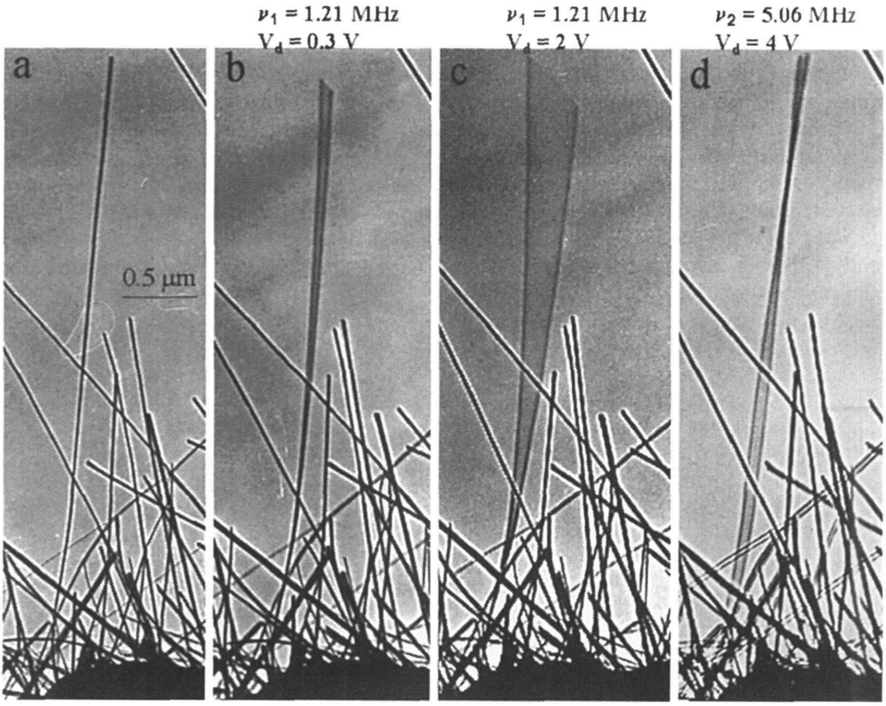
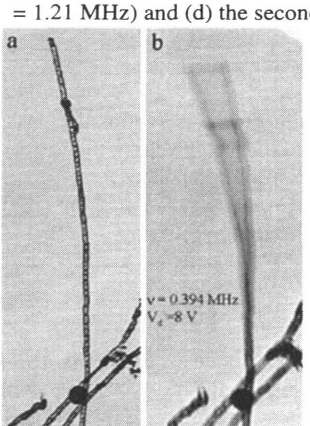


Fig. 2. A selected carbon nanotube at (a) stationary, (b,c) the first harmonic resonance (ν_1 = 1.21 MHz) and (d) the second harmonic resonance (ν_2 = 5.06 MHz).



to be defect-free, the bending modulus is as high as 1.2 TPa (as strong as diamond) for nanotubes with diameters smaller than 8 nm, and it drops to as low as 0.2 TPa for those with diameters larger than 30 nm. A decrease in bending modulus as the increase of the tube diameter is attributed to the wrinkling effect of the wall of the nanotube during small bending. This effect almost vanishes when the diameters of the tubes are less than 12 nm.

Nanotubes produced by catalyst assisted pyrolysis contain a high density of point defects. Figure 3 shows the resonance of a carbon nanotube that exhibits bamboo-like structure. From the resonance frequency, the bending modulus is determined to be 0.03 TPa [6], which is almost 10 times smaller than that of a nanotube without defect, apparently demonstrating the effect of defects on mechanical properties.

Fig. 3. Electro-resonance of a carbon nanotube produced by pyrolysis.

Nanobalance of a single particle

In analogous to a pendulum, the mass of a particle attached at the end of the spring can be determined if the vibration frequency is measured, provided the spring constant is calibrated. If a very tiny mass is attached at the tip of the free end of the nanotube, the resonance frequency drops significantly (Figure 4). The mass of the particle can be thus derived by a simple calculation using an effective mass in the calculation of the inertia of momentum. This newly discovered "nanobalance" has been shown to be able to measure the mass of a particle as small as 22 ±6 fg (1f = 10^{-15}). *This is the most sensitive and smallest balance in the world.* We are currently applying this nanobalance to measure the mass of a single large biomolecule or a biomedical particle.

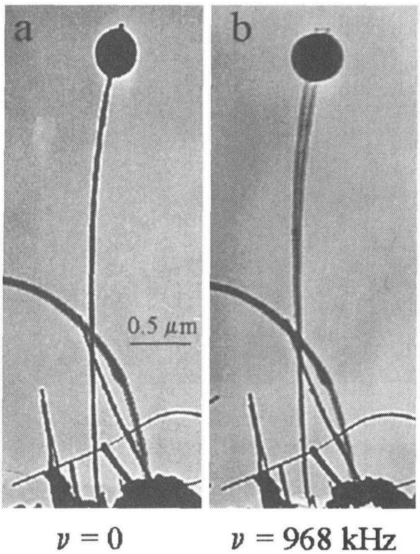


Fig. 4. A small particle attached at the end of a carbon nanotube at (a) stationary and (b) first harmonic resonance ($\nu = 0.968$ MHz). The effective mass of the particle is measured to be ~ 22 fg (1 f = 10^{-15}).

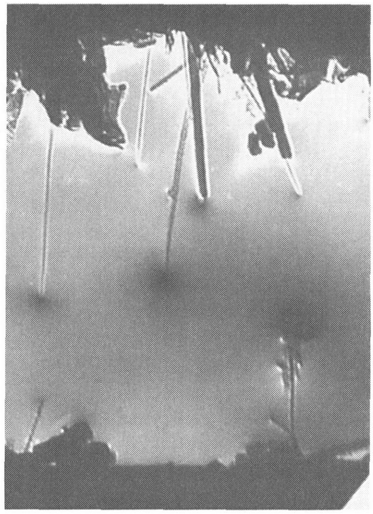


Fig. 5. In-situ TEM observation the electric field induced electron emission from carbon nanotubes. The applied voltage is 60 V and the emission current ~ 20 μA.

Electron field emission from individual carbon nanotubes

The unique structure of carbon nanotubes clearly indicates they are ideal objects that can be used for producing high field emission current density in flat panel display [7]. Most of the current measurements were made using a film of the aligned carbon nanotubes, in which there is a large variation in nanotube diameters and lengths, resulting in difficulty to clearly characterize the true switching-on field for electron field emission. Using the in-situ TEM setup we built, the electric field induced electron emission of a single carbon nanotube has been studied. Figure 5 shows an TEM image of the carbon nanotubes which are emitting electrons at an applied voltage of 60 V. The dark contrast near the tips of the nanotube is the field contributed by the charges on the tip of the nanotube and the emitting electrons. A detailed analysis of the field distribution near the tip of the carbon nanotube by electron holography is being carried out, which is expected to provide the threshold field for field emission and many other properties.

Electric transport properties

We have measured the electric property of a single multi-walled carbon nanotube using the set up of an atomic force microscope (AFM) [8]. A carbon fiber from the arc-discharge chamber was attached to the tip of the AFM, the carbon tube at the forefront of the fiber was in contact with a liquid mercury bath. The conductance was measured as a function of the depth the tube was inserted into the mercury. Surprisingly, the conductance shows quantized steps. The experiment had been repeated in TEM using the in-situ specimen holder. Figure 6 shows the contact of a carbon nanotube with the mercury electrode. The conductance of G_0 was observed for a single nanotube. It is interesting to note that the contact area between the nanotube and the mercury surface is curved. This is likely due to the difference in surface work function between nanotube and mercury, thus, electrostatic attraction could distort the mercury surface.

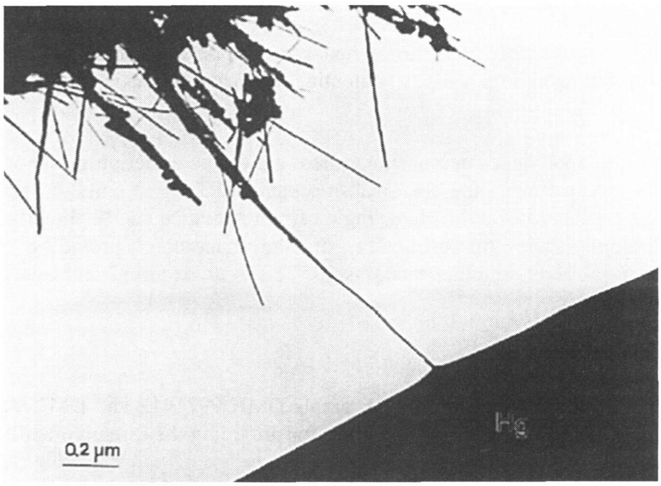


Fig. 6. Conductance of a carbon nanotube measured using the set up in TEM.

To directly find out if some nanotubes are conducting while some are not, we have observed the response of the nanotubes before and after applying a large voltage. Shown in Figure 7 is a case in which there are several nanotubes being in electrical contact at a small voltage/current (Figure 7a). Altering applying a larger voltage of about 10 V, all of the nanotubes but one were burnt out due to the heat generated, indicating that nanotube was non-conducting. This experiment showed the co-existence of conducting and non-conducting/semiconducting nanotubes, in agreement with theoretical prediction.

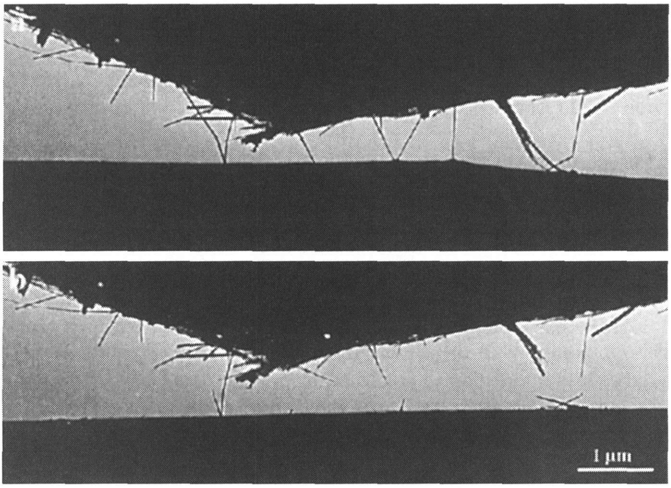


Figure 7. Electrical contact between carbon nanotubes (upper) and the Hg electrode (lower) (a) before and (b) after applying a 10 V potential, showing the existence of semiconducting nanotubes.

In summary, the approaches demonstrated here are a new direction in nanoscience of using in-situ TEM for measurements the electrical, mechanical and field emission properties. In this technique the properties measured from a single carbon nanotube can be directly correlated with the intrinsic atomic-scale microstructure of the nanotube, providing an one-to-one correspondence in property-structure relationship. This is an exciting field towards nanoscience and nanotechnology.

ACKNOWLEDGEMENT

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